

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN THE PRODUCTION OF WHITE MINERAL OIL

- (71) We, ATLANTIC RICHFIELD COMPANY, a corporation organised under the laws of the State of Pennsylvania, United States of America, of Arco Plaza, 515 Flower Street, Los Angeles, State of California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to a process for the production of white mineral oil. More particularly, this invention relates to a two-step catalytic hydrogenation process for producing white mineral oil of high quality and in high yields.
- Various prior art processes have been satisfactory in producing white mineral oils. For example, United States Patent 3,459,656, issued August 5, 1969, describes a two-step catalytic process wherein the second step takes place in the presence of a platinum group metal promoted catalyst. The present invention is directed to an improvement in such a process.
- According to the present invention the improved process comprises first contacting a mineral oil distillate of lubricating viscosity with hydrogen in the presence of a sulfur-resistant catalyst to form a hydrogenated oil having a sulfur content reduced from the sulfur content of the distillate and then second contacting at least a portion of the hydrogenated oil with hydrogen in the presence of a second catalyst to form a refined oil which preferably has specific dispersion reduced from the specific dispersion of the hydrogenated oil from which white mineral oil is recovered; said second catalyst comprising a major amount of a support, a minor, catalytically effective amount of a palladium component and a minor amount of at least one halogen component sufficient to improve the hydrogenation activity of the second catalyst.
- The use of the specified second catalyst leads to significantly improved results e.g. improved catalytic hydrogenation selectivity and activity.
- The process of this invention has been found to be particularly effective in providing technical and food grade white mineral oils of high quality and in high yields, e.g., greater than 90%. Suitable mineral oil distillates of lubricating viscosity for use in the present invention include heavy or light raw distillate oils, for instance obtained by distillation of a naphthenic base light reduced crude such as Gulf Coast and California crudes. The naphthenic oils often have a specific dispersion of at least 130. Waxy lubricating oil distillates from crude oils having a characterization factor (as defined on page 565 of "Chemical Engineers Handbook" edited by John H. Perry, Third edition, published by the McGraw Hill Book Company, Inc., New York, 1950) of at least 11.5, e.g., mixed base and paraffinic crude oils, may also be used in the present invention, for example, as food grade white oil feedstocks. Typically, the mineral oil distillates used in the present invention often have viscosities in the range of 50 SUS to 7500 SUS at 100°F. If the oils contain wax, they are preferably dewaxed prior to the first contacting step, although the dewaxing can follow this step. Dewaxing can be carried out, for example, by using a solvent, such as methyl-ethyl ketone and toluene, to obtain an oil with a pour point (ASTM D 97) below about 25°F. The pour point necessary after dewaxing is determined by that required in the finished oil.
- The first contacting step of the present process is preferably conducted at a temperature within the range from 600°F. to 800°F., more preferably from 650°F. to 725°F.; at a pressure within the range from 1500 psig. to 5000 psig., more preferably from 2000 psig. to 3000 psig.; at a weight hourly space velocity (WHSV) of 0.1 to 1.0, more preferably from 0.25 to 1.0; and at a hydrogen to mineral oil distillate ratio within the range from 1000 s.c.f./b. to 5000 s.c.f./b., more preferably from 1500 s.c.f./b. to 5000 s.c.f./b.

At least a portion of the hydrogenated oil from this first contacting step is subjected to a second contacting. This second contacting preferably occurs at a temperature in the range from 400°F. to 650°F., more preferably from 450°F. to 600°F.; at a pressure in the range from 1500 psig. to 5000 psig., more preferably from 2000 psig. to 3000 psig.; at a WHSV from 0.1 to 1.0, more preferably from 0.25 to 1.0; and at a hydrogen to hydrogenated oil ratio within the range from 500 s.c.f./b. to 5000 s.c.f./b., more preferably from 1500 s.c.f./b. to 5000 s.c.f./b.

The first catalyst of the first contacting step can be any of the sulfur resistant, non-precious metal hydrogenation catalysts some of which are conventionally employed in the hydrogenation of heavy petroleum oils. These catalysts typically comprise a major amount of a support and at least one non-precious metallic component in an amount effective to promote the hydrogenation of the mineral oil distillate. Examples of suitable metallic components include tin, vanadium, chromium, molybdenum, tungsten, iron, cobalt, nickel and mixtures thereof. The catalytic metals can be present in the final catalyst as the free metals or in combined form, such as the oxides and sulfides. Preferably, the first catalyst contains catalytically effective amounts of at least one Group VIB metal, i.e., chromium, molybdenum and tungsten, and at least one Group VIII iron-group metal, i.e., iron, cobalt and nickel. Especially preferred catalysts contain nickel, cobalt and mixtures thereof together with tungsten, molybdenum and mixtures thereof. The Group VIB metal is preferably present in amounts of from 5% to 40%, more preferably from 10% to 30%, by weight of the total catalyst, calculated as the weight of the Group VIB metal oxide. The Group VIII iron-group metals are preferably present in an amount of from 2% to 15%, more preferably from 4% to 10%, by weight of the total catalyst, calculated as the weight of the free metal. Other metals and/or metal compounds in addition to the metal components described above, such as rhenium and germanium, may be included in the first catalyst to improve the properties of the composition.

As aforementioned, the second catalyst of the present invention comprises a major amount of a support; a catalytically effective amount of a palladium component and a minor amount of at least one halogen component present in an amount sufficient to improve the hydrogenation activity of the catalyst. This second catalyst is to be distinguished from the first catalyst in that it is not normally considered to be sulfur-resistant.

The palladium component of this second catalyst may be present as the elemental

metal or as a sulfide, oxide or other combined forms. Preferably, the palladium component comprises from 0.01% to 5.0%, more preferably from 0.1% to 3.0%, by weight of the second catalyst, calculated as elemental palladium.

Although various solid refractory type carriers known in the art may be utilized as a support for the first and second catalysts, the preferred support comprises a major amount of calcined, or otherwise activated, alumina. It is preferred that the alumina have a surface area of from 25 m²/gm. to 600 m²/gm. or more. The support comprises a major proportion of each catalyst, preferably at least 60%, by weight, of the first catalyst, and preferably at least 80%, more preferably at least 90%, by weight of the second catalyst. The alumina may be derived from hydrous alumina predominating in alumina trihydrate, alumina monohydrate, amorphous hydrous alumina and mixtures thereof, which alumina when formed as pellets and calcined, has an apparent bulk density of from 0.60 gm./cc. to 0.85 gm./cc, pore volume from 0.45 ml./gm. to 0.70 ml./gm., and surface area from 50 m²/gm. to 500 m²/gm. The alumina supports may contain, in addition, minor proportions of other well-known refractory inorganic oxides such as silica, zirconia and magnesia. However, the preferred supports are substantially pure alumina derived from hydrous alumina predominating in alumina monohydrate, amorphous hydrous alumina and mixtures thereof. More preferably, the alumina is derived from hydrous alumina predominating in alumina monohydrate.

The alumina supports may be synthetically prepared in any suitable manner and may be activated prior to use by one or more treatments including drying, calcination and steaming. For example, calcination often occurs by contacting the support at a temperature in the range from 700°F. to 1500°F., preferably from 850°F. to 1300°F., for a period of time from one hour to 20 hours, preferably from one hour to 5 hours. Thus, for instance, hydrated alumina in the form of a hydrogel can be precipitated from an aqueous solution of a soluble aluminum salt such as aluminum chloride. Ammonium hydroxide is a useful agent for effecting the precipitation. Control of the pH to maintain it within the values of 7 to 10 during the precipitation is desirable for obtaining a good rate of conversion. Extraneous ions, such as halide ions which are introduced in preparing the hydrogel from its mother liquor and washing the filter cake, with water can, if desired, be removed by filtering the alumina hydrogel. Also, if desired, the hydrogel can be aged, say for a period of several days to build up the concentration of alumina trihydrate in the hydrogel.

The alumina may be formed into macrosized

particles of any desired shape such as pills, cakes, extrudates, powders, granules and spheres, using conventional methods. The size selected for the macrosized particles can be dependent upon the intended environment in which the final catalyst is to be used—as, for example, whether in a fixed or moving bed reaction system. Thus, for example, where as in the preferred embodiment of the present invention, the catalysts are designed for use in reaction systems employing a fixed bed of catalyst, the alumina will preferably be formed into particles having a minimum dimension of at least 0.01 inch. and a maximum dimension up to one-half inch. Or one inch. or more. Spherical particles having a diameter of 0.03 inch. to 0.25 inch., preferably 0.03 inch. to 0.15 inch., are often useful, especially in a fixed bed reactor system.

An essential constituent of the second catalyst of the present invention is a halogen component. Although the precise chemistry of the association of the halogen component with the support, e.g., alumina, is not entirely known, the halogen component may be referred to as being combined with the alumina support or with the other ingredients of the catalyst. This combined halogen may be fluorine, chlorine, bromine, and mixtures thereof. Of these, fluorine and, particularly, chlorine are preferred for the purposes of the present invention. The halogen may be added to the alumina support in any suitable manner, either during preparation of the support, or before or after the addition of the palladium. For example, at least a portion of the halogen may be added at any stage of the preparation of the support, or to the calcined catalyst support, as an aqueous solution of an acid such as hydrogen fluoride, hydrogen chloride or hydrogen bromide or as a substantially anhydrous gaseous stream of these halogen-containing components. The halogen component, or a portion thereof, may be composited with alumina during the impregnation of the latter with the palladium component, for example, through the utilization of a mixture of chloropalladic acid and hydrogen chloride. When the catalyst is prepared by impregnating calcined, formed alumina, for example, spheres, it is preferred to impregnate the support simultaneously with the palladium and halogen. In any event, the halogen is preferably added in such a manner as to result in a fully composited second catalyst that contains from 0.1% to 4.0%, more preferably from 0.6% to 2.5%, by weight of halogen calculated on an elemental basis. During processing, i.e., the period during which hydrogenated oil in the presence of hydrogen is being contacted with the second catalyst, the halogen content of the second catalyst can be maintained at or restored to the desired level by the addition of halogen-containing compounds, such as carbon tetrachloride, ethyl

trichloride or t-butyl chloride, to the hydrogenated oil before such second contacting.

As indicated above, the second catalyst of the present invention contains at least one palladium component.

The palladium component may be incorporated in the catalyst in any suitable manner, such as by coprecipitation or cogellation with the alumina support, ion-exchange with the alumina support and/or alumina hydrogel, or by the impregnation of the alumina support calcination of the alumina hydrogel. One preferred method for adding the palladium component to the alumina support involves the utilization of a water soluble compound of palladium to impregnate the alumina support after calcination. For example, palladium may be added to the support by comingling the calcined alumina with an aqueous solution of chloropalladic acid. Other water-soluble compounds of palladium may be employed as impregnation solutions, including, for example, ammonium chloropalladate and palladium chloride. The utilization of a palladium-chlorine compound, such as chloropalladic acid, is preferred since it facilitates the incorporation of both the palladium component and at least a minor quantity of the halogen component. Following this impregnation, the resulting impregnated support is dried and may be subjected to a high temperature calcination or oxidation procedure at a temperature in the range from 700°F. to 1500°F., preferably from 850°F. to 1300°F., for a period of time from one hour to 20 hours, preferably from one hour to five hours. The major portion of the halogen component may be added to this otherwise fully composited second catalyst by contacting this catalyst with a substantially anhydrous stream of halogen-containing gas.

If desired, the catalysts of the first and second contactings can be hydrogen purged and/or prereduced prior to use by heating in the presence of hydrogen, for example, at temperature of 300°F. to 600°F. for purging and of 600°F. to 1200°F. for prereducing. By prereduction is meant the chemical reaction, i.e., reduction in oxidation state, of at least a portion of the metallic component of the catalyst. Prereduction may be achieved by contacting the catalyst with hydrogen for a period of time of at least one-half (1/2) hour, preferably from 0.5 hour to 10 hours and at a pressure of from 0 psig. to 500 psig.

Following either the first or second contacting step of the present invention the hydrogenated oil and refined oil may be distilled or topped if desired to remove any hydrocracked or other light products to increase the flash point of the oil. The degree of topping desired will depend on the particular lubricating oil fraction being processed and the particular contacting conditions employed.

Thus, the amount of topped overhead that may be taken off in the topping or distillation step after either contacting may often vary from 0 to 50% by volume, with 0 to 10% by volume being preferred.

EXAMPLE

This example illustrates certain of the advantages of the present invention.

A raw heavy lube distillate feedstock was chosen to be treated according to the present invention. This feedstock had the following properties:

Gravity, °API	17.7
Viscosity, SUS at 100°F.	900
Pour Point, °F.	-15
Specific Dispersion	148
Sulfur content, Wt. %	0.25
Nitrogen Content, ppm.	320
Boiling Range, °F.	700-900

This feedstock was first contacted in a fixed bed reaction system with hydrogen in the presence of a commercially available sulfur-resistant non-precious metal catalyst. This catalyst had the following composition and properties:

Support	Alumina
Nickel Content, Wt. %	2.3
Molybdenum Content, Wt. %	15.6
	(calculated as MoO ₃)
Phosphorus Content, Wt. %	1.4
Surface area, m ² /gm.	162
Total Pore Volume, cc./gm.	0.53

This first contacting took place at the following conditions:

Temperature, °F.	650
Pressure, psig.	2500
WHSV	0.25
Hydrogen to Distillate Feedstock, s.c.f./b.	2500

The hydrogenated oil produced by this first contacting was fractionated (or topped) to remove a small amount of light material which had been formed. The portion of this hydrogenated oil boiling from 650°F. to 900°F. (the bottoms cut) had the following properties:

Gravity, °API	22.8
Viscosity, SUS at 100°F.	536
Pour Point, °F.	-15
Specific Dispersion	106.8
Sulfur Content, Wt. %	0.006%
Nitrogen Content, ppm.	5

A second catalyst was prepared as follows. An extrudate of dry, calcined gamma alumina

was formed from boehmite precursor using conventional techniques. This extrudate had a surface area of 194 m²/gm. and a total pore volume of 0.60 cc./gm.

399 gms. of the extrudate was vacuum impregnated at 170°F. with 450 ml. of an aqueous solution containing 17.39 gms. of palladium chloride, 10 ml. of 3 molar hydrochloric acid and 21 ml. of 3 molar nitric acid. The mixture of extrudate and solution was allowed to equilibrate. The impregnated extrudate was vacuum dried for two and one-half hours and then transferred to an oven for additional drying at 230°F. This dried extrudate was calcined by treating this material in a dry blowing air atmosphere at 900°F. for three hours. The product of this calcination, i.e., the final unreduced second catalyst, included 2.0% by weight of palladium, calculated as elemental palladium, and 1.71% by weight of chloride, calculated as elemental chlorine.

200 gms. of this unreduced second catalyst was placed in a fixed bed reaction system. At least a portion of the palladium component was chemically reduced by contacting the unreduced second catalyst with hydrogen, at the rate of 2 s.c.f./hr. at atmospheric pressure and 600°F. for a period of two hours.

The 650-900°F. cut of the hydrogenated oil was contacted with hydrogen in the presence of this second catalyst to form a refined oil at the following conditions:

Temperature, °F.	500
Pressure, psig.	2500
WHSV	0.25
Hydrogen to Hydrogenated oil s.c.f./b.	2500

This refined oil was subjected to a stripping operation to remove light hydrocarbons formed in this second contacting step. The remaining refined oil had the following properties:

Gravity, °API	23.9
Viscosity, SUS at 100°F.	503
Boiling Range, °F.	640-900°F.
Specific Dispersion	98.9
Saybolt Color	30+

The yield of this portion of the refined oil, i.e., technical grade white oil, is about 90% by volume, based on the volume of the raw lube distillate feedstock. This technical grade white oil easily meets or exceeds the ultra-violet absorbance specifications for technical grade white mineral oil.

WHAT WE CLAIM IS:—

1. A process for preparing a white mineral oil from a mineral oil distillate of lubricating viscosity comprising first contacting said distillate with hydrogen in the presence of a

- sulfur-resistant catalyst to form a hydrogenated oil and then second contact at least a portion of said hydrogenated oil with hydrogen in the presence of a second catalyst to form a refined oil from which said white mineral oil is recovered; said second catalyst comprising a major amount of a support, a minor catalytically-effective amount of at least one palladium component and a minor amount of at least one halogen component sufficient to improve the hydrogenation activity of said second catalyst.
2. A process as claimed in claim 1 wherein the palladium component comprises from 0.01% to 5.0% by weight of said second catalyst and said halogen component comprises from 0.1% to 4.0% of said second catalyst.
3. A process as claimed in claim 1 wherein said palladium component comprises from 0.1% to 3.0% by weight of said second catalyst and said halogen component comprises from 0.6% to 2.5% by weight of said second catalyst.
4. A process as claimed in claim 1, claim 2 or claim 3 wherein said second contacting takes place at a temperature within the range from 400°F. to 650°F. at a pressure within the range from 1500 psig. to 5000 psig., at a WHSV within the range from 0.1 to 1.0, and at a hydrogen to hydrogenated oil ratio within the range from 500 s.c.f./b. to 5000 s.c.f./b.
5. A process as claimed in claim 1, claim 2 or claim 3, wherein said second contacting takes place at a temperature within the range from 450°F. to 600°F., at a pressure within the range from 2000 psig. to 3000 psig., at a weight hourly space velocity within the range from 0.25 to 1.0, and at a hydrogen to hydrogenated oil ratio within the range from 1500 s.c.f./b. to 5000 s.c.f./b.
6. A process as claimed in any one of claims 1 to 5 wherein the support of said second catalyst comprises alumina.
7. A process as claimed in claim 5 wherein the alumina is derived from hydrous alumina predominating in alumina monohydrate.
8. A process as claimed in any one of claims 1 to 7 in which said first contacting takes place at a temperature within the range from 600°F. to 800°F., a pressure within the range from 1500 psig. to 5000 psig., a weight hourly space velocity in the range from 0.1 to 1.0, and a hydrogen to mineral oil distillate ratio within the range from 1000 s.c.f./b. to 5000 s.c.f./b.
9. A process as claimed in any one of claims 1 to 7 wherein said first contacting takes place at a temperature within the range from 650°F. to 725°F., at a pressure within the range from 2000 psig. to 3000 psig., at a weight hourly space velocity from 0.25 to 1.0 and at a hydrogen to mineral oil distillate ratio within the range from 1500 s.c.f./b. to 5000 s.c.f./b.
10. A process as claimed in any one of claims 1 to 9 wherein said halogen component is chlorine.
11. A process as claimed in any one of claims 1 to 10 wherein the supports of both first and second catalysts comprise alumina.
12. A process as claimed in claim 11 wherein the support of both first and second catalysts is alumina derived from hydrous alumina predominating in alumina monohydrate.
13. A process for preparing white mineral oil, substantially as hereinbefore described with particular reference to the Example.
14. White mineral oil obtained by a process as claimed in any one of claims 1 to 13.

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